chromatograph (10-ft Apiezon L column, 180°), one major peak (other than solvent) was observed; collection gave a clear oil which is assigned the structure **3,4,5,5,6-pentamethyl-2-methylenecyclohex-** **3-en-1-one (19).** Its infrared spectrum had prominent bands at 1700 (C=O) and 920 cm^{-1} (terminal CH$_2$). Its nmr spectrum is reported in Table I.

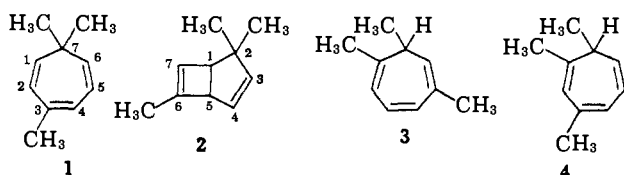# Photolyses of Trienes. Selective Photoreactions of 3,7,7-Trimethylcycloheptatriene

Lee B. Jones and Vera K. Jones

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. Received November 19, 1966

Abstract: Irradiation of a benzene solution of 3,7,7-trimethylcycloheptatriene in a Pyrex tube with a Hanovia high-pressure, mercury arc lamp yields a mixture containing 2,2,6-trimethylbicyclo[3.2.0]hepta-3,6-diene (2), 1,5,7-trimethylcycloheptatriene (3), 1,3,7-trimethylcycloheptatriene (4), and recovered starting material. Compounds 2 and 3 are primary photoproducts while 4 arises from the further irradiation of 3. Under the same conditions, 1-deuterio-3,7,7-trimethylcycloheptatriene gives the corresponding monodeuterated products. The new trienes arise from highly selective [1,7] sigmatropic methyl and hydrogen migrations, and the bicyclic product arises from a selective electrocyclization reaction. The origin of these highly selective transformations is discussed.

Recently, there has been considerable interest in the photoisomerization of various cyclic trienes. Cycloheptatriene photoisomerizes to give the valence tautomer bicyclo[3.2.0]hepta-2,6-diene.[1] Thujic acid and its methyl ester upon irradiation yield 1,7-dimethyl-4-carbomethoxycycloheptatriene (or the corresponding acid) resulting from methyl migration, in addition to 2,2-dimethyl-5-carbomethoxybicyclo[3.2.0]hepta-3,6-diene (or the corresponding acid).[2] The formation of the new triene was rationalized on the basis of a highly polarized excited state. ter Borg and Kloosterziel[3] studied the photolysis of 7-deuteriocycloheptatriene and observed a [1,7] sigmatropic hydrogen migration. Similar [1,7] hydrogen shifts have recently been noted in the photolyses of 1,4-bis(cycloheptatrienyl)benzene isomers.[4]

Our interest in these photolysis reactions led us to investigate the photoisomerization of the readily available 3,7,7-trimethylcycloheptatriene (1),[5,6] as this compound presents interesting possibilities for the pathway of photoisomerization of olefins containing no readily polarizable functional group. We have found that irradiation of 1 in benzene solution with a 450-w Hanovia high-pressure mercury arc lamp for 3-6 hr results in the formation of 2,2,6-trimethylbicyclo[3.2.0]-hepta-3,6-diene (2), 1,5,7-trimethylcycloheptatriene (3), and 1,3,7-trimethylcycloheptatriene (4).

The assignments of structure to the photoproducts are based on spectroscopic data and quantitative catalytic hydrogenation. Hydrogenation of 2 results in the uptake of 2 moles of hydrogen. The ultraviolet spectrum of 2 shows only end absorption [210 mμ (ϵ 2640)] indicating that the double bonds are unconjugated. The nuclear magnetic resonance (nmr) spectrum of 2 shows the *gem*-dimethyl group as two nonequivalent singlets at 0.92 and 0.98 ppm. The vinyl methyl group appears at 1.62 ppm. The bridgehead hydrogens at positions 1 and 5 appear as broad bands at 2.70 and 3.39 ppm, respectively. The cyclopentene hydrogen at position 3 appears as a doublet at 5.25 ppm ($J = 6$ cps) further coupled with the bridgehead hydrogen at position 1 ($J = \sim 1$ cps). The remaining cyclopentene hydrogen and the cyclobutene hydrogen appear as a multiplet at 5.52–5.70 ppm.

The ultraviolet spectra of trienes 3 and 4 show medium intensity bands at 267 mμ (ϵ 3740) and at 266 mμ (ϵ 3750), respectively, which correspond to those shown by other tropilidenes.[6] Quantitative hydrogenation of a mixture containing 55% 3 and 45% 4 results in the uptake of 3 moles of hydrogen. More definitive evidence for the structures of 3 and 4 comes from the nmr spectra. Previous work[6,7] has indicated a characteristic separation of the 1–6, 2–5, and 3–4 pairs of olefin proton absorptions into upfield, midfield, and downfield regions, respectively. The nmr spectrum of 3 shows a three-proton doublet at 1.06 ppm ($J = 7$ cps). The vinyl methyl groups appear as broadened singlets at 1.69 and 1.78 ppm and obscure the absorption of the proton at position 7 which also appears in this region. The olefinic proton absorptions appear at 4.61 ppm (one-hydrogen doublet, $J = 5.5$ cps), at 5.62 ppm (a broad band corresponding to one hydrogen), and at 6.03–6.18 ppm (two-hydrogen multiplet). The nmr spectrum of 4 shows a three-proton doublet at 1.13 ppm ($J = 7$ cps). The vinyl methyl groups appear

(1) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).
(2) O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1961).
(3) A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 241 (1965).
(4) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 3527 (1966).
(5) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **78**, 180 (1956).
(6) J. A. Berson and M. R. Willcott, III, *ibid.* **88**, 2494 (1966).

(7) K. Conrow, M. E. H. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963).

as broadened singlets at 1.80 and 1.90 ppm, obscuring the absorption of the proton at position 7. The olefinic proton absorptions appear at 4.76 and 4.92 (one-hydrogen pair of doublets, J = 6 cps), at 5.55–5.92 (two hydrogen multiplet), and at 5.98–6.20 ppm (one-hydrogen multiplet).

To further substantiate the proposed structures and to gain insight into the mechanism of formation of the photoproducts, we carried out the photolysis of 1-deuterio-3,7,7-trimethylcycloheptatriene. Eucarvone exchanges three hydrogens for deuterium in basic deuterioxylic media to give eucarvone-d_3.[5,6] Since the exchange of the third hydrogen for deuterium occurs at a considerably slower rate than the exchange of the first two hydrogens, eucarvone-d_2 was prepared as starting material for the preparation of 1-d_1. The nmr spectrum of the olefinic hydrogen region of 1-d_1 shows a one-hydrogen multiplet at 4.85–5.15, a 1.7-hydrogen multiplet at 5.70–6.08, and a one-hydrogen multiplet at 6.08–6.30 ppm, indicating that our 1-d_1 was completely deuterated at position 1 and 30% deuterated at position 5.

Photolysis of 1-d_1 was carried out under the conditions used in the unlabeled series. The deuterated products were isolated and the nmr spectra were determined. The nmr spectrum of compound 2-d_1 shows three-hydrogen singlets at 0.94 and 0.99 ppm and a three-hydrogen absorption at 1.62 ppm. A one-hydrogen band appears at 3.37 ppm. The cyclopentene proton at position 3 appears as a doublet at 5.24 ppm (J = 6 cps) and as a singlet at 5.24 ppm as a result of 30% deuterium substitution at position 5 in 1-d_1. The remaining olefinic proton absorptions occur as a 1.7-hydrogen multiplet at 5.50–5.70 ppm. Triene 3-d_1 shows a three-hydrogen absorption at 1.16 ppm [CH$_3$C(D)<]. Two three-hydrogen doublets (J = 1.5 cps) appear at 1.78 and 1.83 ppm (vinyl methyls). The olefinic hydrogen region shows one-hydrogen absorptions at 4.73 and 5.70 ppm in addition to a multiplet at 6.12–6.28 ppm (1.7-hydrogens). The nmr spectrum of 4-d_1 shows a three-hydrogen absorption at 1.20 ppm [CH$_3$C(D)<]. Two three-hydrogen broadened singlets appear at 1.88 and 1.98 ppm (vinyl methyls). One olefinic hydrogen appears as a doublet at 4.90 ppm (J = 9 cps) and as a singlet at 4.90 ppm because of the small amount of deuterium at position 5 of 1-d_1. The remaining olefinic protons appear at 5.60–6.02 (1.7-hydrogen multiplet) and at 6.04–6.30 ppm (one-hydrogen multiplet).

The photolysis of 1 leads ultimately to a mixture consisting of 2, 3, and 4. It has been demonstrated, however, that only 2 and 3 are primary photoproducts. The cycloheptatriene 4 is formed from 3 in a second photochemical process. This was verified by analyzing the photolysis reaction mixture at various time intervals to determine the relative amounts of 3 and 4. The results clearly indicate that in the early stages of reaction 3 is the only new triene formed. The interconvertibility of 3 and 4 is shown by the following results. Irradiation of 3 in benzene for 8 hr resulted in the ratio of 45% 3 and 55% 4. Irradiation of 4 in benzene for 5 hr resulted in the ratio of 40% 3 and 60% 4. Irradiation of 1 in benzene for 9.5 hr resulted in the ratio of 45% 3 and 55% 4 verifying the apparent photoequilibrium of 3 and 4 under the reaction conditions.

Discussion

The photolytic reaction sequence of 1 may be pictured as shown in Scheme I. Starting material 1 is converted directly into 2 and 3. Product 2 is inert to

Scheme I
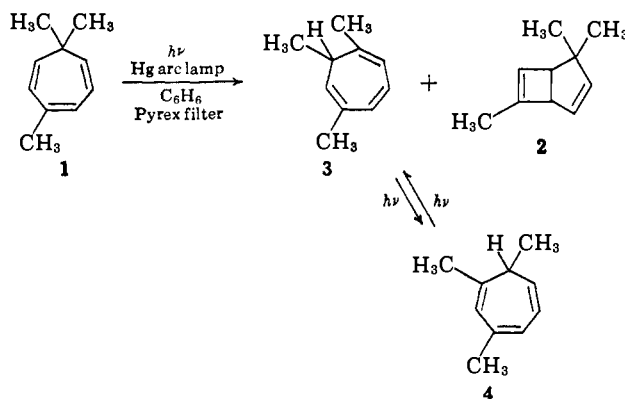
further photochemical reaction but 3 is converted to an equilibrium mixture of 3 and 4. Prolonged irradiation slowly converts 3 and 4 into other products, probably bicyclo[3.2.0] compounds.

The photoreactions observed for 1 are highly specific. Only one of the two possible valence tautomers is produced. The other possibility, compound 5, could not be detected. The methyl and hydrogen migrations noted in these systems are also highly selective. Of the possible methyl shifts only one is observed. The formation of 6 could not be detected. Similarly, it is noted
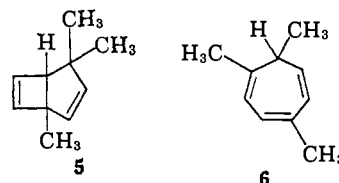
that only one of the possible [1,7] sigmatropic hydrogen migrations is observed (3 ⇌ 4). This clearly demonstrates that the methyl group on carbon atom 3 in the reactant 1 is able to exert an overwhelming directive influence on the course of these photolytic reactions.

The selective formation of photoproduct 3 can be understood by applying the Woodward–Hoffman rules for sigmatropic migrations[8] as well as other molecular orbital considerations to substituted trienes. If one assumes that the transition state of the methyl migration reaction is composed of a radical containing seven π electrons[8] and a methyl radical, one is led to the prediction based on the orbital symmetry of ψ_5 (lowest unfilled molecular orbital of the C$_7$ radical) that migration can take place [1,7] to give either 3 or 6. The possibility of a [1,3] or [1,5] methyl migration is ruled out by these same symmetry considerations[9] because

(8) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 2511 (1965).

(9) It has been pointed out that migration allowed thermal reactions in this system are [1,3]-*antarafacial*, [1,5]-*suprafacial*, and [1,7]-*antarafacial* processes.[8] It is further suggested that these relationships are precisely reversed for sigmatropic changes occurring from a first excited species. This cannot be correct because the symmetry relationships of the molecular orbitals for the unperturbed linear heptatrienyl radical are such that ψ_4 (the highest filled molecular orbital) is an antisymmetric wave function, while ψ_5 (the lowest unfilled molecular orbital) must be symmetric. As a result the symmetry-allowed sigmatropic migrations within the first excited state are [1,3]-*antarafacial*, [1,5]-*antarafacial*, and [1,7]-*suprafacial*.

antarafacial processes are not possible owing to the presence of the ring system.[8] These predictions are based on the assumption that a σ orbital of the migrating methyl group interacts with the π system of the transition state.

The two possible transition states for [1,7] methyl migration are 7 and 8 where the $+$ and $-$ signs indicate the orbital symmetry. A choice between these two

7   8
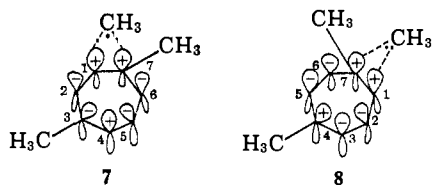
transition states may be made by considering the non-uniform charge distribution present in each transition state. The first excited state of the C_7 radical consists of filled molecular orbitals ψ_1, ψ_2, and ψ_3. ψ_4 is empty and ψ_5 is half-filled. As a result Hückel molecular orbital theory[10] (HMO) predicts a nonuniform charge density in this system for the lowest excited state. The net result of HMO calculations is that in transition state 7 a relatively large positive charge resides on carbon atom 3 which contains the methyl substituent. In transition state 8 a relatively large negative charge is located on the ring carbon bearing this substituent. In each of these two transition states, C-7 which contains the other methyl substituent is, at most, only very slightly positive. The effect of the methyl group is to supply electron density to the ring carbon by an inductive and hyperconjugative interaction mechanism.[11] This has the net effect of increasing the Coulomb integral α[12] for the ring carbon bearing this substituent and tends to stabilize any electron deficiency at this carbon. Similarly, an increased α tends to destabilize those systems in which a negative charge density is located at this carbon. As a result, transition state 7 should represent the lower energy transition state and compound 3 should predominate.

Similarly, considerations of charge density and symmetry arguments[8] indicate that compound 3 upon further irradiation should be transformed selectively into 4. Irradiation of 4 should lead to product 3. These predictions are consistent with our experimental data.

The selectivity noted for [1,7] sigmatropic hydrogen migrations[3,4] in other photochemical systems is similarly explained by a consideration of the Woodward–Hoffmann rules and HMO charge density calculations. The selective [1,7] methyl shift noted in the photolysis of thujic acid (and ester)[2] is satisfactorily accounted for by these considerations.

The selectivity of the electrocyclization reaction to produce 2 is considerably more difficult to explain. Application of the Woodward–Hoffmann rules for electrocyclization reactions[13] indicates that either of the bicyclic compounds (2 and 5) may be formed by a disrotatory cyclization process. Similarly, HMO cal-

culations of charge density (utilizing an increased value of the Coulomb integral α for C-3 in 1) do not allow for a choice between 2 and 5. It has been suggested[14] that a consideration of free valence indices[15] and π-bond orders[16] should allow one to predict the course of cyclization reactions. This approach also fails to account for the selectivity noted for the cyclization process. The only rationalization for the observed selectivity which can be presented at this time involves steric considerations. The formation of 5 would result in a methyl–hydrogen eclipsing interaction in the cyclobutene ring whereas the formation of 2 avoids this interaction by placing the methyl group on one of the trigonal carbons of the cyclobutene ring. In addition, the presence of the methyl group on the unsaturated carbon leads to further stabilization[17] of 2 relative to 5. The cyclopentene ring in 5 contains two methyl groups in a 1,3-*cis* relationship. It is doubtful, however, that this 1,3-dimethyl interaction could be of any great importance, because Dreiding models indicate that the two groups are sufficiently far apart to avoid any serious nonbonded interaction.

A detailed mechanistic investigation of these and other related reactions should more clearly delineate the directive effects of a methyl substituent.

Experimental Section[18]

3,7,7-Trimethylcycloheptatriene (1) was prepared essentially as previously described.[3,4] Following lithium aluminum hydride reduction of 15 g (0.1 mole) of eucarvone, the crude alcohol was distilled from 1 g of potassium hydrogen sulfate at a bath temperature of 120° (20 mm) to give 5.1 g (0.038 mole, 35%) of 1, bp 60–63° (20 mm) [lit.[5] bp 65° (70 mm)].

1-Deuterio-3,7,7-trimethylcycloheptatriene (1-d_1). A mixture of 6 g (40 mmoles) of eucarvone, 30 ml of methanol-d_1,[19] 10 ml of deuterium oxide, and 1 g of sodium methoxide was refluxed for 18 hr. Vhe mixture was cooled and extracted with pentane. The pentane layer was dried and concentrated. The crude eucarvone-d_2 was reduced and dehydrated as described above to give 2.4 g (18 mmoles, 45%) of 1-d_1, bp 63–65° (30 mm) [lit.[6] bp 63–65° (25 mm)].

Irradiation of 3,7,7-Trimethylcycloheptatriene (1). A solution of 1.5 g of 1 in 60 ml of benzene was irradiated in a Pyrex tube with a 450-w Hanovia lamp for 5 hr. The reaction mixture was concentrated at water aspirator pressure and analyzed by gas chromatography[20] to show 56% 2, 9% 1, and 35% of a mixture of 3 and 4, in order of retention times. Further gas chromatography[21] showed 3 and 4 to be present in the relative amounts of 55 and 45%, respectively, in order of retention time. Compounds 2, 3, and 4 were collected.

In a similar reaction, 167.0 mg of 1 was irradiated in 8 ml of benzene for 3.5 hr. The mixture was concentrated and 55.0 mg of *cis*-decalin was added as an internal standard. Upon analysis by

(10) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 142.

(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 204.

(12) Reference 10, p 23.

(13) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965).

(14) Z. Simon, *Zh. Fiz. Khim.*, [6] 38, 1609 (1964); *Chem. Abstr.*, 61, 9084d (1964).

(15) C. A. Coulson, *Discussions Faraday Soc.*, 2, 9 (1947); *J. Chim. Phys.*, 45, 243 (1948).

(16) C. A. Coulson, *Proc. Roy. Soc.* (London), A169, 413 (1939).

(17) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 338.

(18) All boiling points are uncorrected. Magnesium sulfate was employed as a drying agent. Ultraviolet spectra of solutions in 95% ethanol were determined with a Cary Model 14 recording spectrophotometer. Nuclear magnetic resonance spectra of carbon tetrachloride solutions with tetramethylsilane as reference were determined at 60 Mc with a Varian Model A-60 nmr spectrometer. Infrared spectra of carbon tetrachloride solutions were determined with a Perkin-Elmer Model 337 infrared recording spectrophotometer. The microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo.

(19) H. O. House and V. Kramar, *J. Org. Chem.*, 28, 3362 (1963).

(20) A column packed with SE 30 suspended on Chromosorb P was employed.

(21) A column packed with 4-methyl-4-nitropimelonitrile (NMPN) suspended on Chromosorb P was employed.

gas chromatography,[20,21] the calculated yields were 47% **2**, 4% **1**, 22% **3**, and 18% **4**.

Irradiation of 200 mg of **1** in 8 ml of benzene for 9.5 hr followed by gas chromatography[21] showed **3** and **4** to be present in the relative amounts of 45 and 55%, respectively.

Irradiation of 140 mg of **1** in 5 ml of benzene was followed by gas chromatographic analysis[21] at various time intervals to determine the relative amounts of **3** and **4**. The results are listed in Table I.

Table I. Relative Amounts of **3** and **4** during Irradiation of **1**

Time, min	% **3**	% **4**
5	100	0
15	100	0
25	93	7
35	92	8
65	81	19
80	78	22
200	60	40
550	45	55

The nmr and ultraviolet spectra of compounds **2**, **3**, and **4** are described in the text. *Anal.* Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found for **2**: C, 89.42; H, 10.51. Found for a mixture of 55% **3** and 45% **4**: C, 88.71; H, 10.61.[22]

The infrared spectrum of **2** shows a medium band at 3020 cm^{-1} (C–H stretch of olefin) and a weak band at 1640 cm^{-1} (unconjugated double bond).

A 82.3-mg (0.614 mmole) sample of **2** in 10 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 29 mg of platinum oxide. The hydrogen

(22) We could not obtain a satisfactory analysis for **3** and **4**, either separately or as a mixture, despite repeated collections and recollections by gas chromatography,[20,21] followed by short-path distillation. Our only conclusion is that the compounds suffer decomposition prior to analysis. The nmr spectra give satisfactory integrations. The ultraviolet spectra were obtained on samples immediately following collection.

uptake (32.5 cc or 2.1 equiv) ceased after 50 min. The reaction mixture was filtered and concentrated. Gas chromatography[20,23] showed only one peak in addition to the solvent.

A 34.9-mg (0.26 mmole) sample of a mixture of 55% **3** and 45% **4** in 15 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 35 mg of platinum oxide. The hydrogen uptake (20.5 cc or 3.1 equiv) ceased after 40 min. The reaction mixture was filtered and concentrated. Gas chromatography[20,21,23] showed only one peak in addition to solvent. The material was collected for analysis. *Anal.* Calcd for $C_{10}H_{20}$: C, 85.62; H, 14.38. Found: C, 85.79; H, 14.18.

Irradiation of 1-Deuterio-3,7,7-trimethylcycloheptatriene (1-d_1). A solution of 1.5 g of **1**-d_1 was irradiated in 40 ml of benzene as described for the unlabeled compound for 4.5 hr. The reaction mixture was concentrated and samples of **2**, **3**, and **4** were collected by gas chromatography.[20,21]

Photoequilibration of 3 and 4. A. Irradiation of 10 mg of **3** in 0.25 ml of benzene for 8 hr showed **3** and **4** to be present in the relative amounts of 45 and 55%, respectively.

B. Irradiation of 10 mg of **4** in 0.25 ml of benzene for 5 hr showed **3** and **4** to be present in the relative amounts of 40 and 60%, respectively.

Irradiation of 2. A solution of 60 mg of **2** was irradiated in 2 ml of benzene for 24 hr. Gas chromatography[20] showed one peak in addition to solvent having the retention time of **2**.

Irradiation of Trienes 3 and 4. A solution of 40 mg of the trienes (52% **3** and 48% **4**) was irradiated in 2 ml of benzene. After 2 hr, the relative amounts of the trienes were 45% **3** and 55% **4**. This ratio remained unchanged during further irradiation. After 6.5 hr, gas chromatography[20] showed 65% of a new, poorly resolved multiplet containing at least three peaks having retention times very similar to **2**. Irradiation was discontinued after 8.5 hr, at which time gas chromatography[20] showed 95% of new products and 5% of the trienes (still 45% **3** and 55% **4** as determined by gas chromatography[21]). The new products were not investigated further.

(23) A column packed with Carbowax 20M suspended on Chromosorb P was employed.

Cyclic Polyolefins. XLVI. Synthesis of 1,2-Di(hydroxymethyl)cyclooctatetraene and Cyclooctatetraene-1,2-dicarboxylic Acid[1a]

Arthur C. Cope[1b] and Jay E. Meili[1c]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received December 17, 1966

Abstract: 1,2-Di(hydroxymethyl)cyclooctatetraene and 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid have been synthesized by the copolymerization of acetylene with 2-butyne-1,4-diol diacetate and with dimethyl acetylenedicarboxylate, respectively. The structures of the products were related to the known 1,2-dimethylcyclooctane. Attempted resolution of 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid *via* the monoquinine salt and the mono-*d*-α-methylphenethylamine (Dexedrine) salt was unsuccessful.

S ubstituted cyclooctatetraenes have been synthesized by the copolymerization of acetylene and substituted acetylenes[2] under conditions similar to those employed

(1) (a) Abstracted from the Ph.D. thesis of J. E. Meili, Massachusetts Institute of Technology, 1952. (b) Deceased June 4, 1966. (c) Author to whom inquiries should be addressed: Plastocon Corp., Oconomowoc, Wis.

in the preparation of cyclooctatetraene from acetylene.[3,4]

(2) A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.*, **73**, 3536 (1951); **74**, 179 (1952).
(3) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).
(4) A. C. Cope and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72**, 1129 (1950).